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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Aqueous emulsion polymer as dispersant

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Aqueous emulsion polymer as dispersant

This invention relates to an aqueous acrylic emulsion polymer suitable as pigment dispersing agent.

To introduce solid substances, such as pigments, into liquid media, high mechanical forces are necessary. This depends to a large extent on the solid substance's wettability by the surrounding medium, as well as on the affinity for this medium. In order to reduce these dispersing forces, it is conventional to use dispersing agents which facilitate incorporating the substances. This mostly concerns surface-active agents or surfactants, of anionic or cationic or non-ionic structure. In relatively low amounts of addition, these agents are either applied directly to the solid substance or added to the dispersing medium. Through such a surfactant, the energy required for the dispersion is considerably reduced.

Further, it is known that such solid substances, after dispersion, tend to reagglomerate, which nullifies the initially induced dispersing energy and leads to serious problems. This phenomenon can be explained by *inter alia* London/van der Waals' forces, by which the solid substances are mutually attracted. In order to nullify these attractive forces, adsorption layers should be provided on the solid substances. This occurs through the use of such surfactants or polymers.

During and after the dispersion, however, there arises an interaction of the surrounding medium with the solid particle, so that a desorption of the surfactant can arise in exchange for the surrounding medium present in a higher concentration. However, in most cases this surrounding medium is incapable of building up such stable adsorption layers, so that the entire system flocculates. This is evidenced by *inter alia* an increase of the viscosity in liquid systems, loss of gloss, color shifts in paints and coatings, insufficient development of coloring power in pigmented plastics and lacquers, as well as a decrease of the mechanical strength in reinforced plastics.

The International publication WO02/057004 (EFKA Additives B.V.) describes a new range of dispersants based on the use of dendrimers as core material for the dispersing agent. This results in a very specific three-dimensional structure with advantageous dispersing properties. The dispersing agent comprises at least one dendrimer, said dendrimer

comprising functional groups, that have reacted with a functional moiety, said moiety being defined as -R-X, X being a pigment affinic group, and R being a linking moiety chain having at least 2 atoms in the chain, with the proviso that the functional group and the pigment affinic group are different.

United States Patent Application 2002/0132890 describes a water-based acrylic emulsion dispersants for an inorganic pigment. The acrylic emulsion dispersant is the reaction product of butyl methacrylate, butyl acrylate, styrene, methyl ether polyethylene glycol methacrylate, polyethylene glycol methacrylate, and polyphosphoric acid. Thus, an acid anchoring group is present which interacts with metal centers that are inherent in inorganic pigments to stabilise the pigment or pigments in the pigment dispersion.

It is an object of the present invention to provide a water based pigment dispersant in a solvent free environment having improved dispersing properties for organic and inorganic pigments in water based polymer/coatings.

The dispersants of the state of the art are soluble in the medium of the dispersion, e.g. in water. Surprisingly it has been found that a water insoluble system (emulsion) can be used as a dispersant in aqueous systems.

Thus, the invention relates to an aqueous emulsion polymer comprising as co polymerized units the following monomers

- (A) an ethylenically unsaturated monomer containing at least one amino group
- (B) an ethylenically unsaturated monomer containing no amino group
- (C) optionally a hydroxy- or alkoxyalkyl(meth)acrylate of the formula
$$\text{CH}_2=\text{CH}(\text{R}^1)-\text{COO}-\text{C}_t\text{H}_{2t}-\text{OR}^2$$
wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_6$ alkyl and  $t$  is an integer of 2, 3, 4, 5 or 6;
- (D) a (poly)alkyleneglycolmono(meth)acrylate of the formula
$$\text{CH}_2=\text{CH}(\text{R}^1)-\text{COO}-(\text{C}_m\text{H}_{2m}\text{O})_n-\text{OR}^2$$
wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_6$ alkyl and  $m$  is an integer of 2 or 3 and  $n$  is an integer of 2 to 30.

Compound (A) is present in an amount of 0.1- 30 weight % based on the total amount of monomers used.

Compound (B) is present in an amount of 0.1-30 weight % based on the total amount of monomers used

Compound (C) is present in an amount of 0- 50 weight % based on the total amount of monomers used.

Compound (D) is present an amount of 0.1- 50 weight % based on the total amount of monomers used.

The total numbers of monomer is 100 weight %.

In a preferred embodiment compound (C) is present.

### Definitions

The term "aqueous emulsion polymer" refers to a water dispersed or emulsified polymer with water being the medium or a mixture of water and a water soluble/miscible organic solvent.

Non- limiting examples for **ethylenically unsaturated monomers containing at least one amino group (Group A )** are:

Amino(meth)acrylates such as N,N-dimethylamino-methyl(meth)acrylate, N,N-dimethyl-amino-ethyl(meth)acrylate, N,N-diethylamino-ethyl(meth)acrylate;

Amino (meth)acrylamides such as for example, N,N-dimethylaminoethyl (meth)acrylamide, N,N-diethylaminoethyl (meth)acrylamide, N, N-dimethylaminopropyl (meth)acrylamide, N-methylol(meth)acrylamide; (meth)acrylonitril;

Heterocyclic vinyl compounds for example vinylpyridines such as 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine; N-vinyl-pyrimidine, N-vinylpiperidine, 2-vinylpiperidine, 4-vinylpiperidine, N-vinylpiperazine, N-vinylpiperidone, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrole, N-vinylpyrazole, N-vinylpyrrolidone, 2-vinyl-pyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, , N-vinylmorpholine, N-vinyloxolane, N-vinylfuran, N-vinylthiophene, N-vinylthiolane, N-vinyl-1,2,3-triazole, N-vinyl-1,2,4-triazole, N-vinyl-1,3,4-triazole and hydrogenated vinylthiazoles, vinyl-oxazoles and hydrogenated vinyloxazoles



Preferred are amino(meth)acrylates and heterocyclic vinyl compounds, especially vinylpyridines and vinylimidazoles of the latter.

Non-limiting examples of suitable ethylenically unsaturated monomers containing no amino group (Group B) are:

Alkyl vinyl ethers, such as, for example, methyl vinyl ether, isopropyl vinyl ether, isobutyl vinyl ether, vinyl 2-methoxy ethyl ether, n-propyl vinyl ether, t-butyl vinyl ether, isoamyl vinyl ether, n-hexyl vinyl ether, 2-ethylbutyl vinyl ether, diisopropylmethyl vinyl ether, 1-methyl-heptyl vinyl ether, n-decyl vinyl ether, n-tetradecyl vinyl ether, and n-octadecyl vinyl ether;

Gamma substituted ethers, such as, for example, alpha-methylvinyl methyl ether, .alpha.-methylvinyl ethyl ether, .alpha.-amylvinyl methyl ether, and .alpha.-phenylvinyl ethyl ether;

Alicyclic and aralkyl vinyl ethers such as, for example, cyclohexanol vinyl ether, menthol vinyl ether, carvacrol vinyl ether, benzyl alcohol vinyl ether, .beta.-phenylethanol vinyl ether, tetrahydronaphthol vinyl ether, .beta.-decahydronaphthol vinyl ether, methylphenyl carbinol vinyl ether, butyl-cyclohexanol vinyl ether, and dihydroabictinol vinyl ether;

Vinyl aryl ethers such as, for example, vinyl phenyl ether, .alpha.-bromovinyl phenyl ether, .alpha.-phenylvinyl phenyl ether, vinyl m-cresyl ether, .alpha.-methyl vinyl p-cresyl ether, vinyl p-chlorophenyl ether, vinyl 2,4,6-trichlorophenyl ether, and vinyl .alpha.-naphthyl ether;

Vinyl esters of linear or branched carboxylic acids such as, for example, vinyl acetate, vinyl methoxyacetate, vinyl trimethylacetate, vinyl isobutyrate, isopropenyl butyrate, vinyl lactate, vinylcaprylate, vinyl pelargonate, vinyl myristate, vinyl oleate, vinyl linoleate, vinylversatate;

Vinyl esters of aromatic acids, such as, for example, vinyl benzoate, vinyl alkoxybenzoates, vinyl octylphthalate, vinyl tetrachlorobenzoate, vinyl beta-phenyl butyrate, vinyl beta-naphthoate, and vinyl ethyl phthalate;

Vinyl formate and vinyl carbonate derivatives such as, for example, vinyl formate, vinyl chloroformate, methylvinyl chloroformate, vinyl methyl carbonate, vinyl ethyl carbonate, vinyl phenylcarbonate and vinylidenecarbonate;

Vinyl thioesters such as, for example, vinyl methyl sulphide, vinyl n-butyl sulphides, 1-chloroethyl vinyl sulphides, 2-chloroethyl vinyl sulphide, vinyl dodecyl sulphide, vinyl phenyl sulphide, vinyl o-cresyl sulphide, vinyl 2,5-dimethyl-4-chlorophenyl sulphide, vinyl 8-chloro-naphthyl sulphide, and vinyl 2-benzothiazylsulphide.

Styrene and related monomers such as, for example styrene, o-methylstyrene, p-methylstyrene, 3,4-dimethyl styrene, 2,4,6-trimethyl styrene, m-ethyl styrene, 2,5-diethyl styrene,

p-butyl styrene, m-t-butyl styrene, p-benzyl styrene, o-methoxy styrene, p-methoxystyrene, 6-methoxy-3-methyl styrene, 2,6-dimethoxy styrene, and 2-methoxy-5-isopropyl styrene;

Derivatives of alpha-methyl styrene, such as, for example, 4-chloro alpha-methyl styrene, 3,4-dimethyl alpha-methylstyrene, 3-bromo-2-methyl alpha-methylstyrene, and 2,5-dichloro-alpha-methylstyrene;

Chlorostyrene derivatives, such as, for example, m-chlorostyrene, 2,3-dichlorostyrene, 3,4-dichlorostyrene, trichlorostyrene, and pentachlorostyrene;

Bromo- and fluorostyrene derivatives, such as, for example, p-bromostyrene, m-fluorostyrene, m-trifluoromethyl styrene, 4-fluoro-3-trifluoromethyl styrene, and pentafluorostyrene;

Other styrene derivatives such as, for example, p-formyl styrene, methyl ester of p-vinyl benzoic acid, p-vinylbenzyl alcohol, 1,4-dimethyl-2-hydroxystyrene, 3,5-dibromo-4-hydroxystyrene, 2-nitro-4-isopropylstyrene;

Vinyl derivatives of biphenyl, naphthalene and related aromatic compounds, such as, for example, 4-chloro-4'-vinyl biphenyl, o-isopropenyl biphenyl, p-vinyl diphenyl oxide, 4-chloro-1-vinyl naphthalene, 1-chloro-4-vinyl naphthalene and 1-vinyl acinaphthalene;

Vinylfuran, vinylbenzofuran, vinylthiophene such as, for example, 2-vinyl dibenzofuran, 5-ethyl-2-vinyl-thiophene, 5-chloro-2-vinyl thiophene, 3,4,5-trichloro-2-vinyl thiophene and 2-vinyl dibenzothiophene;

Ethylene and chloro-, fluoro- and cyano- derivatives of alkylene, such as, for example, ethylene, vinylchloride, vinylidene-chloride, vinylfluoride, vinylidene fluoride, tetrafluoroethylene, trifluorochloroethylene, hexafluoropropylene;

Acrylate and methacrylate monomers such as, for example, acrylate, methylacrylate, ethylacrylate, propylacrylate, isopropyl acrylate, n-, sec-, t-butylacrylate, 3-methyl-1-pentylacrylate, octylacrylate, tetradecylacrylate, 2-ethylhexyl acrylate, and phenyl acrylate; methacrylate, methyl methacrylate, n-propyl methacrylate, n-, sec-, t-butyl methacrylate, 2-ethylhexyl methacrylate 2-methyl cyclohexyl methacrylate, monofluoroethyl methacrylate, beta.-bromoethyl methacrylate, o-cresyl methacrylate, beta-naphthyl methacrylate, acrylic acid, methacrylic acid,

Alpha.-halogen acrylates, such as, for example, methyl chloro acrylate, methyl bromo acrylate, ethyl chloro acrylate, s-butyl chloro acrylate, cyclohexyl chloro acrylate, phenyl chloro acrylate, cyclohexyl bromo acrylate, n-propyl chloro acrylate, isopropyl chloro acrylate, n-butylchloro acrylate, and methyl fluoro acrylate;

Dienes particularly 1,3-butadiene, isoprene, and chloroprene, 2-fluoro-butadiene, 1,1,3-tri-

fluorobutadiene, 1,1,2,3-tetrafluoro butadiene, 1,1,2-trifluoro-3,4-dichlorobutadiene and tri- and pentafluoro butadiene and isoprene; and the like.

Preferred monomers include alkyl(meth)acrylate units and/or (meth)acrylic acid and/or other vinylic compounds capable of forming polymerisable radicals (e.g. styrene, n-propyl methacrylate, 2-methyl cyclohexyl methacrylate, tert-butylacrylate, iso-butyl methacrylate, iso-butyl acrylate, o-cresyl methacrylate, t-butyl methacrylate, n-butyl acrylate, n-butyl methacrylate, methylacrylate, methyl methacrylate, ethylacrylate, propylacrylate, iso-propyl methacrylate, 3-methyl-1-pentylacrylate, octylacrylate, tetradecylacrylate, s-butylacrylate, s-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, 2-methoxyethyl acrylate, phenyl acrylate, acrylic acid, methacrylic acid 1,3-butadiene, isoprene, p-methylstyrene, 3,4-dimethyl styrene, m-ethyl styrene, p-butyl styrene, o-methoxy styrene, p-methoxystyrene, 2,6-dimethoxy styrene, vinyl acetate, vinyl methoxyacetate, vinyl isobutyrate, vinyl oleate, vinyl benzoate, vinyloctylphthalate.

Non-limiting examples of hydroxy- or alkoxyalkyl(meth)acrylates (Group C) are: 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 2-hydroxy-n-butyl acrylate and 2-hydroxy-n-butyl methacrylate and their corresponding methyl-, ethyl-, propyl- and butylethers or acetates.

Non-limiting examples of (poly)alkyleneglycolmono(meth)acrylates (Group D) are diethylene glycol monoacrylate, diethylene glycol monomethacrylate, triethylene glycol monoacrylate, triethylene glycol monomethacrylate, pentaethylene glycol monoacrylate, pentaethylene glycol monomethacrylate, dipropylene glycol monoacrylate, dipropylene glycol monomethacrylate, tripropylene glycol monoacrylate, tripropylene glycol monomethacrylate, pentapropylene glycol monoacrylate and pentapropylene glycol monomethacrylate; and their corresponding methyl-, ethyl-, propyl- and butylethers or acetates.

C<sub>1</sub>-C<sub>4</sub> alkylethers of (poly)alkyleneglycolmono(meth)acrylates such as methoxypolyethylene-glycolmethacrylate and the like.



### Use

The aqueous acrylic emulsion polymer can be used as a dispersing agent in aqueous systems, especially for organic or inorganic pigments in an aqueous medium; for water-based coatings or to produce Resin Free Pigment Concentrates for ultra low VOC coatings.

Thus, it is a further object of the invention to provide a pigment dispersion comprising inorganic or organic pigments and an aqueous emulsion polymer as described above.

Thus, the present invention also relates to a pigment dispersion comprising at least one organic and/or inorganic pigment; water and/or a mixture of water and water miscible solvents and an emulsion polymer comprising as copolymerized units the following monomers::

- (A) an ethylenically unsaturated monomer containing at least one amino group
- (B) an ethylenically unsaturated monomer containing no amino group
- (C) optionally a hydroxy- or alkoxyalkyl(meth)acrylate of the formula  
$$\text{CH}_2=\text{CH}(\text{R}^1)-\text{COO}-\text{C}_t\text{H}_{2t}-\text{OR}^2$$
wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_8$ alkyl and  $t$  is an integer of 2, 3, 4, 5 or 6;
- (D) a (poly)alkyleneglycolmono(meth)acrylate of the formula  
$$\text{CH}_2=\text{CH}(\text{R}^1)-\text{COO}-(\text{C}_m\text{H}_{2m}\text{O})_n-\text{OR}^2$$
wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_8$ alkyl and  $m$  is an integer of 2 or 3 and  $n$  is an integer of 2 to 30.

Suitable dispersible organic pigments are selected from the azo pigment group consisting of azo, disazo, naphthol, benzimidazolone, azocondensation, metal complex, isoindolinone, and isoindoline pigments, the chinophthalon pigment, dioxazine pigment and the polycyclic pigment group consisting of indigo, thioindigo, quinacridones, phthalocyanines, perylenes, perionones, anthraquinones, such as aminoanthraquinones or hydroxyanthraquinones, anthrapyrimidines, indanthrones, flavanthrones, pyranthrones, anthantrones, isoviolanthrones, diketopyrrolopyrrole, and carbazoles, e.g. carbazole violet, pigments, pearlescent flakes and the like. Further examples of organic pigments can be found in the monograph: *W. Herbst, K. Hunger "Industrielle organische Pigmente" 2<sup>nd</sup> Edition, 1995, VCH Verlagsgesellschaft, ISBN: 3-527-28744-2.*

Suitable dispersible inorganic pigments are selected from the group consisting of metallic flakes, such aluminum, aluminum oxide, calcium carbonate, silicon oxide and silicates, iron(III)oxide, chromium(III)oxide, titanium(IV)oxide, zirconium(IV)oxide, zinc oxide, zinc sulfide, zinc phosphate, mixed metal oxide phosphates, molybdenum sulfide, cadmiumsulfide, carbon black or graphite, vanadates, such as bismuth vanadate, chromates, such as lead(IV)chromate, and molybdates, such as lead(IV)molybdate, and mixtures, crystal forms or modifications thereof, such as rutil, anatas, mica, talcum or kaoline.

Water-miscible solvents are for example, C<sub>1</sub>-C<sub>4</sub>alkohols, e.g. methanol, ethanol, or isopropanol, polyols, e.g. glycerol, or ethylene or propylene glycols, their dimers, trimers or polymers and their corresponding C<sub>1</sub>-C<sub>4</sub> alkylethers.

The aqueous emulsion polymer according to the invention can be added, as dispersants in amounts of 0.1 to 200 weight percentage of solid dispersant to the pigment. The optimum activity of the polymer compound according to the invention is obtained at concentrations of 0.5 to 5 weight percentage of solid dispersant to inorganic pigment and 10 to 200% weight percentage of solid dispersant to organic pigment.

Optimum results are obtained at concentrations of 1.5 to 3 weight percentage of solid dispersant to inorganic pigment and 25 to 100 weight percentage of solid dispersant to organic pigment.

The dispersants can also be used in the form of such salts, which are obtained by neutralization of the polymer with organic acids. Alternatively the polymer can be quaternized with alkylating agents such as benzylbromide, benzylchloride, methyl iodide, dimethylsulfate, diethylsulfate and the like.

The emulsion polymer of the invention can be used alone or in combination with other high or low molecular weight dispersants or in combination with a suitable synergist.

Different types of synergists can be used to accommodate the different use conditions of the polymer. Non-limiting examples of synergists are commercially available dispersants sold under the trade name **SOLSPERSE** 5000 and 22000 from Avecia, Inc. of Wilmington or EFKA-6745, EFKA-6746 and EFKA-6750, produced by EFKA Additives B.V..

High molecular weight dispersants are, for example, dispersants based on polyurethane such as EFKA-4520® or modified polyacrylates, such as EFKA-4500®, produced by EFKA Additives B.V.

Low molecular weight dispersants are, for example, dispersants based on fatty acid modified polyesters such as EFKA-6220® produced by EFKA Additives B.V.

Further common additives may be present such as defoamers, preservatives, anionic type wetting agents such as EFKA-6230® and EFKA-8510®, cationic wetting agents such as EFKA -5071®, leveling agents such as EFKA-3030®, EFKA-3034® and EFKA-3035®, anti cratering agents such as EFKA-3570 and EFKA 3580 and coalescing solvents such as glycols, glycolethers and the like.

Defoamers which may be utilized include, for example EFKA-2550, EFKA 2526 and EFKA-2527 produced by EFKA Additives B.V.

Preservatives which may be utilized include Metatin K521 produced by Rohm and Haas.

#### **Preparation of the emulsion polymer**

The aqueous acrylic emulsion polymer is prepared using known polymerization methods as described in patent DE 19 12 483 and U.S. 4.170.582.

A suitable process for preparing an aqueous emulsion polymer as described above comprises the steps of:

- (i) mixing the monomers (A), (B), (C), (D) and an initiator (E); or mixing the monomers (A), (B), (C), (D), water and an initiator (E) to establish a premix;
- (ii) adding the premix into water containing an initiator (E),
- (iii) polymerizing the premix to obtain the emulsion polymer.

The polymerization time depends on the temperature and the desired final product properties but is preferably within the range of from 0.5 to 10 hours at temperatures at a range from 25°C and 150 °C, more preferably between 70 °C and 90 °C.

As radical polymerization initiators the usual free radical initiators can be used. Examples are oil-soluble and water soluble initiators such as azobisisobutyronitrile, 2,2'-azobis[2(2-imidazolin-2-yl)propane]dihydrochloride, potassium persulfate, sodium persulfate, ammonium persulfate, tert-butyl peroxy maleic acid, succinic acid peroxide, and tert-butyl hydroperoxide, benzoylperoxide, di-tertiarbutylperoxide, tertiarybutylperoxybenzoate, tertiarybutylperoxy-2-ethylhexanoate and the like.

The initiator is present in step (i) and in step(ii) of the above process. The suitable amount of polymerization initiator in step (i) is from 0.1 to about 5% by weight on the basis of the total amount of the monomers used.

The dispersion preferably contains a surfactant, that may be included in the premix phase or water phase or both phases. Preferably, the surfactant is combined with the monomers in the premix phase.

**Suitable surfactants** which may be used include ionic and nonionic surfactants. Typical examples are:

Alkyl polyglycol ethers such as, for example, ethoxylation products of lauryl, tridecyl, oleyl, and stearyl alcohols;

Alkyl phenol polyglycol ethers such as, for example, ethoxylation products of octyl- or nonylphenol, diisopropyl phenol, triisopropyl phenol;

Alkali metal or ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, and the like, including sodium lauryl sulfate, sodium octylphenol glycoether sulfate, sodium dodecylbenzene sulfonate, sodium lauryldiglycol sulfate, and ammonium tritertiarybutyl phenol and penta- and octa-glycol sulfonates,

Sulfosuccinate salts such as, for example, disodium ethoxylated nonylphenol half ester of sulfosuccinic acid, disodium n-octyldecyl sulfosuccinate, sodium dioctyl sulfosuccinate, and the like.

The suitable amount of surfactant is from 0.1% to about 2 % by weight percentage on the basis of the total amount of the monomers used.

Thus the above process comprises the steps of

(i) mixing the monomers (A), (B), (C), (D), water, an initiator (E) and a surfactant (F) to establish a premix;

- (ii) adding the premix into water containing an initiator (E) and a surfactant (F),
- (iii) polymerizing the premix to the emulsion polymer.

It is also possible to adjust the molecular weight of the resulting polymer by adding to the premix such a compound as ally alcohol,  $\alpha$ -methyl styrene dimer, n-octylmercaptane, n-dodecylmercaptane, thioglycol acid, iso-octylmercaptopropionate, butylmercaptopropionate and the like. The suitable amount of chain transfer agent is from 0.1% to about 8 % by weight percentage on the basis of the total amount of the monomers used.

Thus, the above process comprises the steps of

- (i) mixing the monomers (A), (B), (C), (D), water, an initiator (E), a surfactant (F) and a chain transfer agent (G) to establish a premix;
- (ii) adding the premix into water containing an initiator (E) and a surfactant (F)
- (iii) polymerizing the premix to the emulsion polymer.

### **Advantages**

The single step premix addition results in a stable polymer dispersion having a low viscosity, good mechanical stability as well as good storage stability.

The emulsion polymer of the invention has a wide-spread compatibility with the resin in most commonly used water-based coatings. Typical examples of which are alkyd -emulsions, acrylic copolymer emulsions and polyurethane dispersions.

The emulsion polymer of the invention has excellent pigment dispersing properties for most commercially available organic pigments such as, for example, azo pigments, phthalocyanine based pigments, quinacridone and diketo-pyrrolo-pyrrole pigments.

The pigment concentrates show no viscosity increase after a storage of several weeks at elevated temperatures, give no settling with inorganic pigments in the aqueous medium and have much higher colour development for organic and inorganic pigments compared to known commercially available dispersing agents for the aqueous medium.



## Examples

### Example 1

Water (383.1 g) and sodium dodecylbenzene sulfonate (0.012 g, 0.012% of the total formulation) were placed in a three-necked flask under a nitrogen atmosphere and heated to 80 °C. At 80 °C a solution consisting of 2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride (3.6 g, 0.0111 mol) and water (20.0 g) was added to the reactor. After 5 minutes the continuous stirred premix consisting of styrene (132.2 g, 1.269 mol), hydroxyethylmethacrylate (54.1 g, 0.416 mol), dimethylaminoethylmethacrylate (56.0 g, 0.356 mol), methoxypolyethyleneglycolmethacrylate (50% solution in water)\* (315.1 g, 0.1459 mol), sodium dodecylbenzenesulfonate (0.06 g, 0.06% of the total formulation), iso-octylmercapto-propionate (19.7 g, 0.090 mol), 2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride (10.90 g, 0.0337 mol), was added during 120 minutes. After addition of the premix, the contents of the flask were stirred for another 120 minutes at 80 °C. The product was a white-yellowish, semi translucent liquid. The measured molecular weight (Mw, GPC, THF, 10% solution) of the prepared polymer was approximately 7000 g/mol.

\* = commercial name Bisomer S10W, Laporte Performance Chemicals

### Analytical data

Appearance	Opalescent liquid
Solid content	43 %
Amine value	22 mg KOH/g
Density at 20 °C	1.05 g.cm <sup>-3</sup>
Viscosity	200 mPa.s

In the following examples a similar polymerization procedure was followed:

Example 2:

Chemical Name	%
Dimethylaminoethylmethacrylate	5.60
Hydroxyethylmethacrylate	5.41
Styrene	13.22
Methoxypolyethyleneglycolmethacrylate (50 % solution in water)*	31.51
Isooctyl 3-mercaptopropionate	1.97
Demi Water	40.753
2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride	1.465
sodium dodecylbenzenesulphonate	0.072

\* = commercial name Bisomer S7W, Laporte Performance Chemicals

Example 3:

Chemical Name	%
Vinylimidazole	4.94
Hydroxyethylacrylate	4.76
MMA	12.37
Methoxypolyethyleneglycolmethacrylate (50 % solution in water)*	28.74
Dodecylmercaptane	0.47
Demi Water	46.668
2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride	1.98
Sodium dodecylbenzenesulphonate	0.072

\* = commercial name Bisomer S10W, Laporte Performance Chemicals

Example 4:

Chemical Name	%
Dimethylaminoethylacrylate	5.60
Hydroxyethylmethacrylate	5.41
Styrene	13.22
Methoxypolyethyleneglycolmethacrylate (50 % solution in water)*	31.51
Isooctyl 3-mercaptopropionate	1.97
Demi Water	40.753
2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride	1.465
Dodecylbenzenesulphonic acid, sodium salt (SDBS)	0.072

\* = commercial name Bisomer S10W, Laporte Performance Chemicals

Example 5:

Chemical Name	%
1-Vinylimidazole	3.36
Hydroxyethylacrylate	5.82
Styrene	14.03
Methoxypolyethyleneglycolmethacrylate*	16.80
Isooctyl 3-mercaptopropionate	2.70
Demi Water	53.218
2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride	4.00
Dodecylbenzenesulphonic acid, sodium salt (SDBS)	0.072

\* = commercial name Bisomer MPEG 550 MA, Laporte Performance Chemicals

**Example 6:**

Chemical Name	%
2-Vinylpyridine	5.60
Hydroxyethylmethacrylate	5.41
Styrene	13.22
Methoxypolyethyleneglycolmethacrylate (50 % solution in water)*	31.51
Isooctyl 3-mercaptopropionate	1.97
Demi Water	40.753
2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride	1.465
Dodecylbenzenesulphonic acid, sodium salt (SDBS)	0.072

\* = commercial name Bisomer S10W, Laporte Performance Chemicals

**Example 7:**

Chemical Name	%
Dimethylaminoethylmethacrylate	5.60
Hydroxyethylacrylate	5.16
Styrene	12.44
Methoxypolyethyleneglycolmethacrylate*	16.80
Isooctyl 3-mercaptopropionate	2.47
Demi Water	53.808
2,2'-Azobis[2(2-imidazolin-2-yl)propane]dihydrochloride	3.65
Dodecylbenzenesulphonic acid, sodium salt (SDBS)	0.072

\* = commercial name Bisomer MPEG 550 MA, Laporte Performance Chemicals

## Application Examples

### 1. Formulations

The organic pigment concentrates are prepared according the following table:

	Comparative	Inventive 1	Inventive 2
Emulsion polymer example 1	0.00	15.60	0.00
Emulsion polymer example 5	0.00	0.00	16.30
Comparative (EFKA 4550)	29.00	0.00	0.00
EFKA 8530	0.00	0.00	1.56
EFKA 2550 (Defoamer)	0.30	0.30	0.30
Demi water	35.60	41.00	38.74
Preservative	0.10	0.10	0.10
Heliogen Blue L 7080 (Pigment)	35.00	43.00	43.0
Total	100.00	100.00	100.00

EFKA 4550 is a high molecular weight polyacrylic compound which is a clear solution. The product is commercially available. It is not an emulsion polymer.

The organic pigment concentrate paste is ground for 2 hours with two parts by weight of glass beads (2-3 mm) to a fineness of  $< 5\mu\text{m}$  in the Scandex.

#### Stability of the organic pigment concentrate at 40°C

	Comparative	Inventive 1	Inventive 2
1 week	+	++	++
2 weeks	0	+	+
3 weeks	0	+	+
4 weeks	0	0	0

Explanation results:

+ = good                      no settlement, no separation  
0 = reasonable              settlement, slightly separated  
- = bad                        a lot of settlement, separated



Viscosity stability of the organic pigment concentrate at 40°C measured with Bohlin Rheometer PP40 (layer thickness 150 µm).

	Comparative	Inventive 1	Inventive 2
Initial	903 mPa.s	192 mPa.s	210 mPa.s
4 weeks	731 mPa.s	241 mPa.s	250 mPa.s

## 2. Use of the organic pigment concentrate

The organic pigment concentrate is added to a satin laquer (20 weightpercent titandioxid).

The ratio between the organic pigment and the titandioxid is 1:25.

The coloured satin laquer is prepared according the following table

	comparative 1	inventive 1	inventive 2
Millbase I	0.0	0.4	0.0
Millbase II	0.0	0.0	0.4
Millbase III	0.4	0.0	0.0
Satin laquer (20 wt% Titandioxide)	17.5	22.5	22.5

After homogenization the laquer is drawdown onto a polyester film with a filmthickness of 75 µm. The film is dried in air for 24 hours.

	color development
comparative	0
inventive 1	+
inventive 2	+

\* = Gloss at 60° minus gloss at 20°

Explanation results

+ = good

0 = reasonable

- = bad

### 3. Preparation of an inorganic pigment concentrate

**The organic pigment concentrate is prepared according the following table:**

	Comparative 2	Inventive 3	Inventive 4
Comparative	15.00	0.00	0.00
Emulsion polymer example 2	0.00	16.30	0.00
Emulsion polymer example 5	0.00	0.00	16.30
EFKA 8530	0.00	1.56	1.56
EFKA 2550 (Defoamer)	0.30	0.30	0.30
Optigel SH	0.30	0.30	0.30
Demi water	24.30	14.44	38.74
Preservative	0.10	0.10	0.10
Bayferrox 130 M (Pigment)	60.00	67.00	67.00
Total	100.00	100.00	100.00

**The inorganic pigment concentrate is ground for 2 hours with two parts by weight of glass beads (2-3 mm) to a fineness of  $< 5\mu\text{m}$  in the Scandex.**

### Stability of the organic pigment concentrate at 40°C

	Comparative 2	Inventive 3	Inventive 4
1 week	+	++	++
2 weeks	+	+	+
3 weeks	0	+	0
4 weeks	-	0	0

**Explanation results:**

**+ = good**                      **no settlement, no separation**

0 = reasonable settlement, slightly separated

- = bad                      a lot of settlement, separated

Viscosity stability of the organic pigment concentrate at 40°C measured with Bohlin Rheometer PP40 (layer thickness 150 µm).

	Comparative	Inventive 1	Inventive 2
Initial	867 mPa.s	192 mPa.s	210 mPa.s
4 weeks	1057mPa.s	241 mPa.s	250 mPa.s
separation	yes	no	no

#### 4. Use of the inorganic pigment concentrate

The organic pigment concentrate is added to a satin laquer (20 weight percent titandioxid).

The ratio between the organic pigment and the titandioxid is 1:10.

The coloured satin laquer is prepared according the following table

	Comparative 2	Inventive 3	Inventive 4
Pigment concentrate comparative 2	0.7	0.0	0.0
Pigment concentrate inventive 3	0.0	0.6	0.0
Pigment concentrate inventive 4	0.0	0.0	0.6
Satin laquer (20 wt% Titandioxide)	21.0	20.1	20.1

After homogenization the laquer is drawn down onto a polyester film with a film thickness of 75 µm. The film is dried in air for 24 hours.

	color development
comparative	0
inventive 1	+
inventive 2	+

#### Explanation results

+ = good

0 = reasonable

- = bad

### Claims

1. An aqueous emulsion polymer comprising as copolymerized units the following monomers

(A) an ethylenically unsaturated monomer containing at least one amino group;

(B) an ethylenically unsaturated monomer containing no amino group;

(C) optionally a hydroxy- or alkoxyalkyl(meth)acrylate of the formula



wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_6$ alkyl and  $t$  is an integer of 2, 3, 4, 5 or 6;

(D) a (poly)alkyleneglycolmono(meth)acrylate of the formula



wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_6$ alkyl and  $m$  is an integer of 2 or 3 and  $n$  is an integer of 2 to 30.

2. An aqueous emulsion polymer according to claim 1 wherein monomer (A) is an amino(meth)acrylate, a vinylpyridine or a vinylimidazole.

3. The use of the aqueous emulsion polymer according to claim 1 as dispersing agent in aqueous systems.

4. The use of the aqueous emulsion polymer according to claim 1 as dispersant for organic and/or inorganic pigments.

5. A pigment dispersion comprising at least one organic and/or inorganic pigment; water and/or a mixture of water and a water miscible solvent and an emulsion polymer according to claim 1.

6. A process for preparing an aqueous emulsion polymer as defined in claim 1, which process comprises the steps of:

(i) mixing the monomers (A), (B), (C), (D) and an initiator (E); or mixing the monomers (A), (B), (C), (D), water and an initiator (E) to establish a premix;

(ii) adding the premix into water containing an Initiator (E),

(iii) polymerizing the premix to the emulsion polymer.

**7. A process for preparing an aqueous emulsion polymer as defined in claim 1, which process comprises the steps of**

**(i) mixing the monomers (A), (B), (C), (D), water, an initiator (E) and a surfactant (F) to establish a premix;**

**(ii) adding the premix into water containing an initiator (E) and a surfactant (F),**

**(iii) polymerizing the premix to the emulsion polymer; or the steps of**

**i) mixing the monomers (A), (B), (C), (D), water, an initiator (E), a surfactant (F) and a chain transfer agent (G) to establish a premix;**

**(ii) adding the premix into water containing an initiator (E) and a surfactant (F)**

**(iii) polymerizing the premix to the emulsion polymer.**



**Abstract:**

This invention relates to an aqueous emulsion polymer used as pigment dispersing agent comprising as copolymerized units the following monomers

- (A) an ethylenically unsaturated monomer containing at least one amino group;
- (B) an ethylenically unsaturated monomer containing no amino group;
- (C) optionally a hydroxy- or alkoxyalkyl(meth)acrylate of the formula  
$$\text{CH}_2=\text{CH}(\text{R}^1)-\text{COO}-\text{C}_t\text{H}_{2t}-\text{OR}^2$$
wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_6$ alkyl and  $t$  is an interger of 2, 3, 4, 5 or 6;
- (D) a (poly)alkyleneglycolmono(meth)acrylate of the formula  
$$\text{CH}_2=\text{CH}(\text{R}^1)-\text{COO}-(\text{C}_m\text{H}_{2m}\text{O})_n-\text{OR}^2$$
wherein  $\text{R}^1$  is hydrogen or methyl and  $\text{R}^2$  is hydrogen or  $\text{C}_1$ - $\text{C}_6$ alkyl and  $m$  is an interger of 2 or 3 and  $n$  is an interger of 2 to 20.

PCT Application  
**EP0312582**



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